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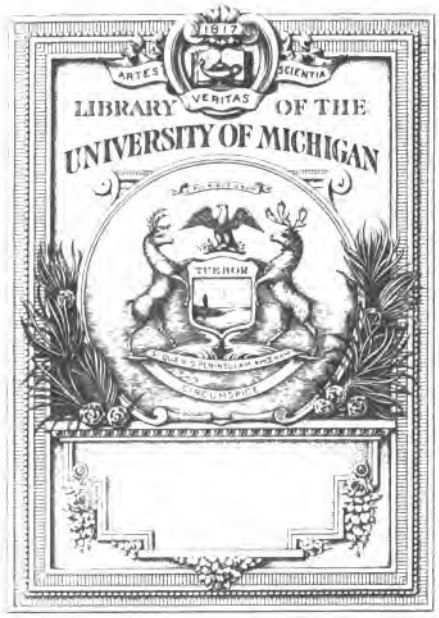

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THE THERMOELECTRIC BEHAVIOR OF HEUSLER ALLOYS IN A MAGNETIC FIELD

BY

L. O. GRONDAHL AND S. KARRER

DIFFRACTION GRATING METHOD FOR DETERMINING INDEX OF REFRACTION

BY

FREDERICK A. OSBORN AND HORACE H. LESTER

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THE THERMOELECTRIC BEHAVIOR OF HEUSLER ALLOYS IN A MAGNETIC FIELD.

BY L. O. GRONDAHL AND S. KARRER.

THE effect of a magnetic field on thermoelectric behavior has been studied by a number of experimenters and with a variety of results. The lack of agreement and of complete data on the subject led the authors to prepare for some experiments on the effect of direction, magnitude, and the nature of the field. The statement by Guthe and Austin[1] that they had looked for the effect in Heusler alloys and that there was none found as great as .5 microvolt, together with the interesting theoretical bearing attributed to it, made it seem worth while to look for the effect with a more sensitive arrangement of apparatus. So the other experiments were postponed and the present report deals almost entirely with the work on the alloys, the results of which seem sufficiently interesting to warrant publication at this time. Investigation of the other points mentioned will be continued.

The method adopted is the same as that employed by Guthe and Austin.[2] As shown by the diagram, Fig. 1, the greater part of the E.M.F. of the couple is balanced by means of a storage cell and a potentiometer. The galvanometer is a low resistance Broca, the sensibility varying around 5×10^{-7} volts per cm., the scale being at a constant distance of about 2.25 meters. R_1 and R_2 are Leeds and Northrop decade boxes. The field current was varied by means of a lamp bank rheostat. The coil used in the preliminary experiments gave a maximum field of about 400 gauss. For the later experiments another coil was built for which the constant at the center was calculated at 114.7. It was 35 cm. long, 4 cm. internal diameter, and 20 cm. external diameter. It was built of No. 9 copper wire and had a short time capacity of about 25 amperes, giving a maximum field of about 2,800 gauss. Calculation gave for the

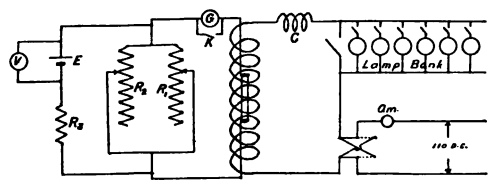

Fig. 1.

[1] B. of S. Bul., Vol. II., No. 2, p. 315, 1906.

[2] Loc. cit.

field at 5 cm. away from the center on the axis, $H = 114.1I$, showing a fairly uniform field for at least 10 cm. along the axis. Theresults with the two coils were found to agree throughout. The field coil was placed about 10 meters away from the galvanometer and its field at the galvanometer was neutralized by means of another solenoid, C, in series with it, and placed near the galvanometer. The effect of the field coil was by this means neutralized so that for no current did it give a deflection greater than .5 mm. on the scale. The galvanometer and all the leads were carefully insulated to avoid grounds or leaks from the field current. K is a key used for short-circuiting the galvanometer to prevent large inductive throws while opening or closing the field circuit.

The junctions of the couple were kept, one in steam and one in circulating ice water, as indicated in Fig. 2. The water was kept moving through about 15 feet of lead pipe imbedded in cracked ice. A propeller driven by a small motor and fitted into a part of the water circuit, served as pump. The temperature constancy obtained by this means is indicated by the constancy of the zero reading as given under "zero" in Table II. The greatest variation for the whole run is 2.2 cm., corresponding to a temperature variation of .2° C. During one reading the temperature was usually constant to a few hundredths of a degree. A layer of asbestos and paper wound on the glass tube served as electrical and heat insulation.

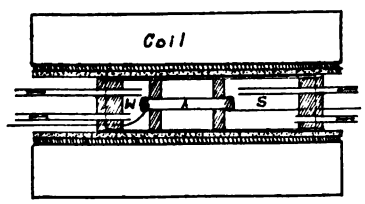

Fig. 2.

The arrangement of electrical apparatus is in principle the same as the deflection potentiometer described by Brooks.[1] A calculation similar to his shows that the galvanometer current is proportional to the difference between the two E.M.F.'s and inversely proportional to the total resistance of the galvanometer circuit. Since the latter is practically constant during an experiment, the sensibility in volts per centimeter deflection was obtained by slightly varying either R_1 or R_2, the E.M.F. of the couple being kept constant. Then

$$S = \frac{E}{d}\left(\frac{R}{R_3 + R} - \frac{R'}{R_3 + R'}\right),$$

where d is the deflection in centimeters caused by the change in R; E, the E.M.F. of the storage cell; R and R', the values of $\frac{R_1R_2}{R_1 + R_2}$ before

[1] B. of S. Bul., Vol. II., No. 2, p. 225, 1906.

and after the change; R_3, a constant resistance of 10,000 ohms. Experiment showed the sensibility to be practically constant over the whole scale and the effect could therefore be read in scale divisions.

The temperature of the coil rose to some extent during an experiment. The constancy of the zero and the fact that a Cu-Zn couple and a Cu-Al couple showed no effect whatever, seemed sufficient proof that the change in temperature of the coil had no appreciable effect on the couple. A Pt-PtIr couple placed in the same position in steam also showed no effect of the change in temperature of the coil. The effect of permanent magnetism, if present in the alloys, is thought to be negligible as far as these experiments are concerned. In the case of all the couples tested, al least two runs were made immediately following one another, and with the field in opposite directions, yet no consistent difference was found even in the small readings, although in the experiments performed no attempt was made to demagnetize between readings. In the Fe-Cu couples it was found necessary to demagnetize partly in order to duplicate the readings with low values of the field. An attempt will be made to investigate the effect of permanent magnetism further.

For the specimens of Heusler alloys we are indebted to Professor A. A. Knowlton, of the University of Utah, who kindly lent us some of the rods prepared by him in 1908 and which he described in the REVIEW.[1] In what follows, the alloys are numbered the same as there. Table I. gives the chemical composition, density, magnetic property, total E.M.F., and range of transformation, for all of which, except the column under E.M.F., we are also indebted to Knowlton. All the alloys show a trace of iron.

A bar of electrolytic iron from Professor C. F. Burgess, University of Wisconsin, a bar each of "purest" nickel and cobalt from Dr. Schuckardt, of Görlitz, and a bar of pure nickel from Kahlbaum, were kindly

TABLE I.

Specimen.	Cu	Mn	Al	Si	Density.	Magnetic Property.	E.M.F.	Transformation Range.
2	67.2	22.5	10.0	.25	6.77	Good.	.00087	225°–275° C.
3	64.9	22.0	12.6	.49	6.83	"	.00075	"
5	65.0	25.8	8.8	.40	6.86	"	.00076	"
8	56.4	29.6	13.1	.89	6.94	Poor.	.00077	"
11	70.4	19.0	9.4	1.22	7.13	"	.000367	40°–120° C.
13	72.6	20.1	7.05	.23	7.16	Medium.	.000383	"
14	72.2	17.4	10.3	.08	7.17	Poor.	.000234	10°– 30° C.

[1] PHYS. REV., Vol. XXXII., p. 54, 1911.

diameter. The couple was made in each case by winding a piece of N 18 copper wire around each end and soldering them to make good contac In the case of the alloys an effort was made to raise the temperature little as possible. Soft solder was used and heated just sufficiently make it possible to spread it with the iron, thus getting a good stead contact without a really soldered junction.

The process of taking an observation consisted in noting the zero the galvanometer, closing the field circuit, noting galvanometer readin opening the field circuit and again determining the zero reading. Th zero used was the mean of the two zero readings. A curve was gotten b taking a series of such observations increasing the current by steps. Al the curves plotted are the averages of at least two such series taken witl the field current in opposite directions. A sample set of observations i given in Table II. The fifth and sixth columns are calculated from the first four, the seventh and eighth are corresponding values obtained afte the current is reversed. E is obtained by multiplying the sensibility o the galvanometer by the deflection. H is obtained from a curve between ammeter reading and field and is approximately $114.5I$. The first column gives the uncorrected ammeter reading.

The results for the alloys are represented by the curves of Fig. 3,

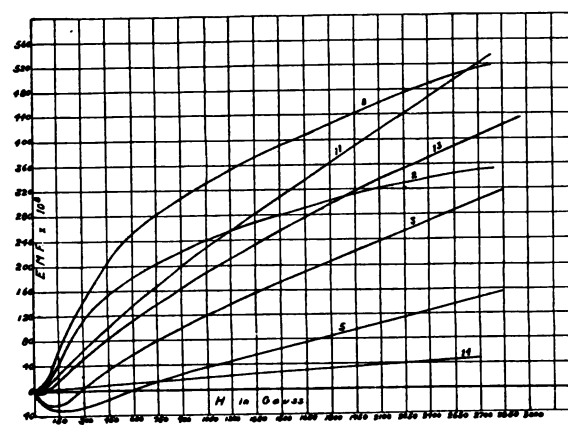

Fig. 3.

those of the magnetic metals by those of Fig. 4. The ordinates represent change in E.M.F.; the abscissæ represent the field. Positive ordinate means an increase, negative a decrease in the E.M.F. As is seen, the effect is found in all the alloys and the shape of the curves is in each case similar to that of some one of the magnetic metals. There seems to be no definite relation between the magnitude of the effect and the magnetic

property of the alloys. The curves of Nos. 3 and 5 which are labeled by Knowlton "Good" in magnetic properties cross the axis, as does also that of the one labeled "Medium," No. 13. These three also seem to approach a maximum earlier than the others. Nos. 11, 13, and 14 all have low transformation points, and during the experiment, one end was probably magnetic, the other not. Whether or not, in that case, the field affected only the end at the lower temperature has not yet been determined. As seen in Table I., the E.M.F. of these alloys is about one half of that shown by those of the high transformation points, and

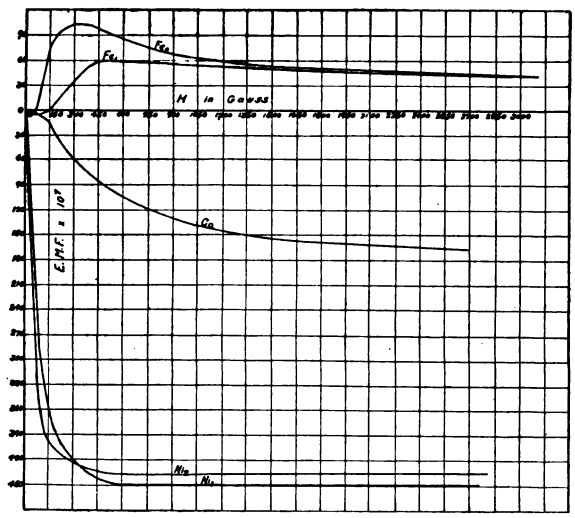

Fig. 4.

yet the change in E.M.F. seems to approach a higher maximum in No. 11 than in any of the rest. It may be seen also, that these curves are more nearly linear than the rest. The shape of those curves which do not cross the line is very similar to that of the magnetostriction curves of Guthe and Austin.[1] One of the authors hopes to investigate the magnetostriction curves of these samples during the coming year. The magnitude of the effect in iron and nickel agrees fairly well with the results obtained by Bidwell[2] who reports a maximum of 30×10^{-6} for nickel and between 6×10^{-6} and 12×10^{-6} for different specimens of iron. For the Al-Cu and the Zn-Cu couples no effect is found as great as 10^{-7} volts.

[1] Loc. cit.

[2] Roy. Soc. Proc., 73, p. 413, June, 1904.

RESULTS.

1. The experiments show that the effect of the magnetic field on thermoelectric behavior is present in Heusler alloys, and is of the same nature as in the case of the magnetic metals.

2. The surmise that the magnetic property of the alloys is different in nature from that of iron, loses its support as far as the present phenomenon is concerned.

3. In this type of field no effect is found in the non-magnetic substances tried, aluminium and zinc. In view of Posejpal's work the effect of the nature of the field on these is to be investigated further.

4. For very low fields the effect in the case of iron samples tried is negative.

PHYSICS LABORATORY,
UNIVERSITY OF WASHINGTON,
August, 1911.

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ACTION GRATING METHOD FOR DETERMINING INDEX OF REFRACTION.

BY FREDERICK A. OSBORN AND HORACE H. LESTER.

IE method here described for determining the index of refraction of a liquid is believed to be new. The index of refraction of the l is determined by finding the ratio of the wave-lengths in air and ıe liquid, by means of a Rowland plane grating, using an Abbe .trometer. The equation for determining λ is given by

$$m\lambda = 2d \sin \theta,$$

l for finding μ, if d is constant,

$$\mu = \frac{\lambda_a}{\lambda_\omega} = \frac{\sin \theta_a}{\sin \theta_\omega},$$

rhere the subscripts refer to the air and liquid values respectively. 3ut the value of d changes with the temperature because of the thermal expansion of the speculum metal of the grating.

Let t_1 be the change in the temperature of the grating for the air readings, from the temperature when d_0 was determined;

t_{11}, the corresponding change in temperature for the liquid readings;

α, the coefficient of expansion of the grating.

Then

$$\mu = \frac{d_0(1 + \alpha t_1) \sin \theta_a}{d_0(1 + \alpha t_{11}) \sin \theta_\omega} = \frac{\sin \theta_a}{\sin \theta_\omega}\left[1 + \alpha \frac{(t_1 - t_{11})}{1 + \alpha t_{11}}\right]$$

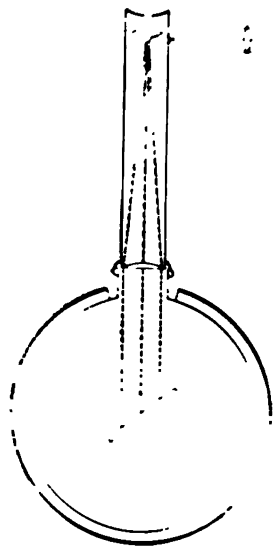
$$= \frac{\sin \theta_a}{\sin \theta_\omega}[1 + \alpha(t_1 - t_{11})] \text{ approx.}$$

Since t_{11} does not differ much from t_1 and t_{11} α is small in comparison to unity.

APPARATUS AND METHOD.

In the Abbe spectrometer (Fig. 1) the functions of the collimator and observing telescope are united. The plane grating, mounted on the rotating table, receives the light from the objective and returns the diffracted light along the same path as the incident light, so that it strikes the plane side of the objective lens, normally, thus avoiding any correction for refraction at the objective.

A Rowland grating of approximately 15,000 lines to the inch w
used. The grating was mounted on the end of the movable spindle. F



2. A double-walled metal tank was mount
on the fixed circle of the spectrometer a
shown, so the grating could be completel
immersed in the liquid, which was distille
water. A heating coil was wound on the out-
side of the tank and then the whole was
wrapped with several layers of asbestos.
Water, placed in the space between the
double walls, helped to hold the temperature
in the grating chamber more nearly constant.
The work was done near 20° C.

The temperature of the inner chamber was
obtained by a thermometer reading directly to
[illegible] C., which had been recently calibrated
by the Bureau of Standards. A stirrer, motor
[illegible] was agitated.

A [illegible] with the aid of
[illegible] that the ther-
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The readings in air and in water for the various lines were made as in the usual grating method for finding μ.

Table I. gives the results as obtained by the authors at different times, working separately and together.

TABLE I.

Line.	t_1	θ_a	t_{11}	θ_ω	μ_t	Corrections.	$\mu_{20°}$	Experimenter.	Order of Spectrum.
H 656	19.5°	35°38′18″	20°	25°57′30″	1.33115	−1	1.33114	Lester	3d
	19.7	18	19.8	27	18	−2	16	Lester	3d
	19.8	17	20°	30	14	0	13	Lester	3d
	20.2	17	20°	30	14	0	14	Lester	3d
	20.3	16	19.9	29	14	−1	13	Lester	3d
	20.5	15	19.6	24	20	−4	16	Lester	3d
							Mean 1.33114−		
Na 5,896	20°	20°25′34″.7	20	15°16′41″.5	1.33299	0	1.33299	Lester	2d
	20°	35		40	302	0		Lester	Apr. 6
		35		40	302	0		Lester	to
		36		40	303	0		Lester	Apr. 26
		35		40.7	302	0		Lester	
		34.7		41	299	0		Lester	
		35.5		40	299	0		Lester	
		34.7		40	301	0		Lester	
		35		40.2	302				
							Mean 1.33301		
Na 5,890	18	31°31′55″	20.4	23°5′53″	1.33305	−5 +4	1.33304	Lester	3d
	20	20°24′14″	20	15°9′40″	04	0	304	Lester	2d
	20	16	20	39	06	0	06	Lester	
	20	14	20	41	03	0	03		
	20	14	20	40	04	0	04		
	20	14	20	41	03	0	03		
	19.2		20.3	39	02	−1 +3	04		
							Mean 1.33304		
Na 5.893							1.333025		

Line.	t_1	θ_a	t_{11}	θ_{aa}	μ_t	Corrections.	$\mu_{20°}$	Experimenter.	Order of Spectrum.
Hg									
579	20.3	30°56′22″	20.1	22°40′55″	1.33328	+1	1.33329	Osborn	3d
	20.2	25	20.1	55	32	1	33	Osborn	3d
	20.3	23	20.1	53	35	1	36	L.	3d
	20	23	20.1	52	33	1	34	L.	3d
	20	23	20.1	52	33	1	34	O. & L.	3d
	20	21	20.1	52	32	1	33	O. & L.	3d
									Dec. 26–29
							Mean 1.33333		
Hg									
577	20	30°48′54″	20.1	22°35′34″	1.33340	+1	1.33341	O.	3d
	20	53	20.1	34	40	1	41	O.	3d
	20	53	20.1	32	43	1	44	L.	3d
	20	52	20.1	33	41	1	42	L.	Dec. 28–30
	20	53	20.1	34	40	1	41	O. & L.	
	20	53	20.1	34	40	1	41	O. & L.	
							Mean 1.333416		

Line.	t_1	θ_a	t_{11}	θ_{aa}	μ_t	Corrections.	$\mu_{20°}$	Experimenter.	Order of Spectrum.
Hg									
546	20.8	29° 0′ 7″	20.5	21°18′14″	1.33439	5	1.33444	S. & M.	3d
	19.9	29 0 9	19.8	13	50	1	51	S. & M.	
	20.0	29 0 8	20	16	49	0	49	O.	
	20.1	29 0 7	20	17	43	0	43	O.	
	19.2	28 59 59	19.8	10	48	3	45	L.	
	19.4	29 0 1	19.8	8	52	2	50		
	19.2	29 0 1	19.8	8	51	3	48		
	20.0	29 0 0	20.8	15	40	8	48		
							Mean 1.33447		
H									
486	22.7	25°34′ 7″	21.9	18°50′ 3″	1.33689	20	1.33712	L.	3d
	22.6	8	21.9	2	93	21	17	L.	
	22.7	16 43 18	21.9	12 25 41	92	21	13	L.	
	22.6	17	22.1	40	93	22	15	L.	2d

Line.	t_1	θ_α	t_{11}	θ_ω	μ_t	Corrections.	μ_{20}	Experimenter.	Order of Spectrum.
Hg 436	20	31° 3′45″	20.1	22°38′30″	1.34031	−1	1.34032	O.	4th
	20	44	19.9	28	33	−1	32	O.	4th
	20	43	20.1	30	26	−1	27	L.	4th
	20	39	19.9	28	30	−1	29	L.	4th
	20	43	19.9	29	29	−1	30	O. & L.	Dec. 26–29
	20	44	20.1	29	31	−1	30	O. & L.	
		44	19.9	28	29	−1	30		
	20.1	22 45 57	20	15 46 54	28	0	28	L.	3d
	20.1	58	20	53	30	0	30	L.	March
	20.1	57	20	52	29	0	29	L.	March
	20.1	57	20	54	28	0	28	L.	March
							Mean 1.340295		

In reducing our values from μ_t to μ_{20} the empirical equation of Flatow, ($\mu_t = \mu_0 - 10^{-5}(at + bt^2 + ct^3 + dt^4)$ was used, where a, b, c, d are the constants, differing for each wave-length. Martens[1] has calculated the values of du/dt for $t = 20°$ and for λ varying from .000214 to .000589. From these values a curve was plotted and the corrections to be applied to our data were taken directly from the curve. The correction due to the expansion of the grating ($\alpha = .000019$) amounts to 2×10^{-6} for a temperature difference of 0.1° C.

Accuracy of the Method.

θ_α and θ_ω were found to $\pm$ 1.5″ and this gives an error in μ of $\pm 2 \times 10^{-5}$. The temperature of the grating was known to $\pm$ .02° C. and an error of this amount affects μ by $\pm 2 \times 10^{-7}$. The temperature of the bath was not in error by .05° C. and this would change μ by $\pm 5 \times 10^{-6}$. The probable error in μ is therefore $\pm 2 \times 10^{-5}$.

Table II. gives the various values for μ_{20} for the wave-lengths worked with, as found by other workers and other methods,[2] and those obtained by our new method. The curve, Fig. 3, which is drawn from the mean values for μ_{20} obtained from the values found by the different workers, shows the variation in their values from the mean and also the position on the mean curve of our values.

Summary.

1. A new method for finding μ for some liquids has been found.
2. The method is simple in theory and practice.

[1] Landolt-Bornstein, Phys.-Chem. Tab., 1905, pp. 669–670.
[2] Landolt-Bornstein, Phys.-Chem. Tab., 1905, pp. 669–670.

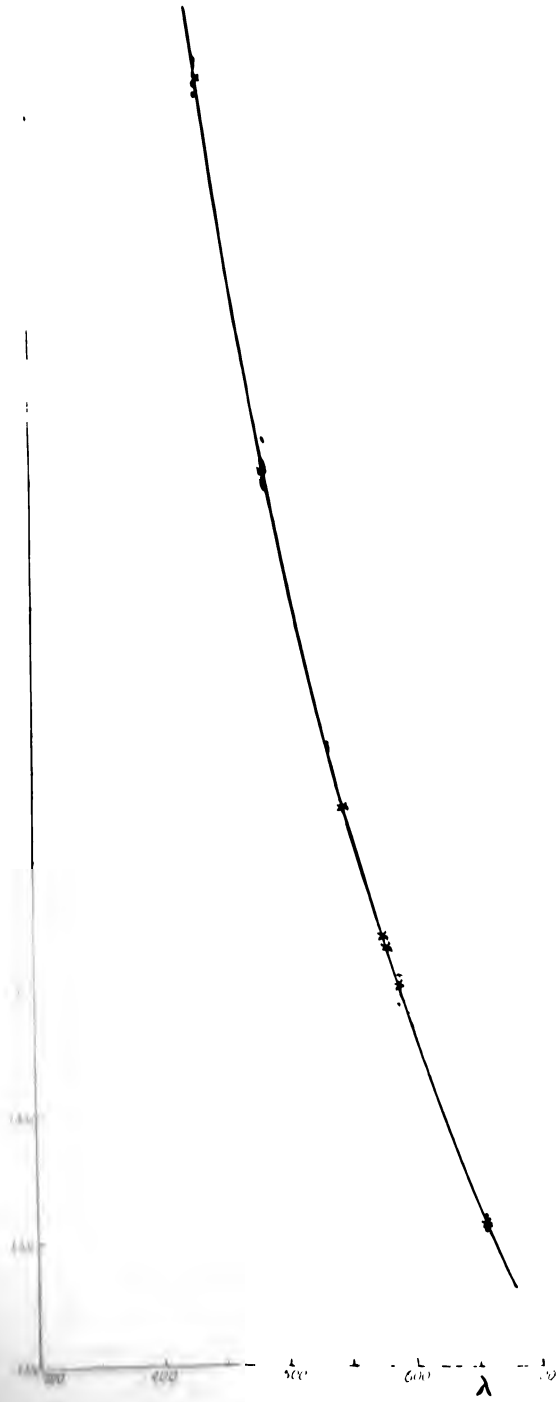

Fig. 3.

Values from new method of $dN/d\lambda$ are indicated by crosses; values from other workers are indicated by dots.